

# Nanoscale Phase Separation in Ferroelectric Materials

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**Abstract** Many materials exhibit nanoscale phase separation, when inside the host thermodynamic phase there arise nanosize embryos of another thermodynamic phase. A prominent example of this phenomenon is provided by ferroelectric materials. The theoretical description of such phase heterogeneous materials is quite challenging, since they are essentially nonuniform, the nonuniformity is random, and often they are quasiequilibrium, but not absolutely equilibrium. An approach is suggested for the theoretical description of phase separated ferroelectrics, consisting of a ferroelectric matrix with nanoscale paraelectric inclusions. The properties of the heterophase ferroelectrics are studied.

**Keywords** Nanoscale phase separation · Ferroelectric materials · Phase transition · Sound velocity · Debye-Waller factor

## 1 Features of Nanoscale Separation

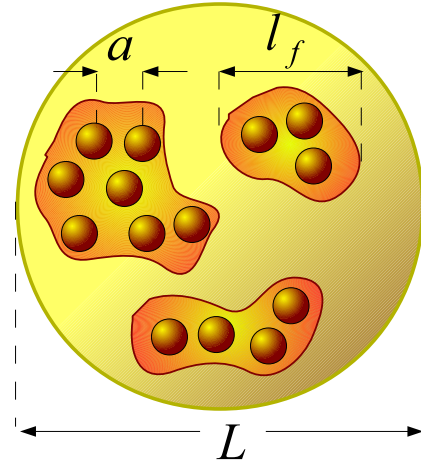
There exists quite a number of materials exhibiting the so-called nanoscale phase separation, when in the bulk of one phase there occur nanosize germs of another phase. The schematic picture of such a heterophase matter is illustrated in Fig. 1. The typical sizes of the heterophase inclusions  $l_f$  are much larger than the interparticle distance  $a$ , but much smaller than the linear size of the sample  $L$ ,

$$a \ll l_f \ll L,$$

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because of which this phase separation is termed *mesoscopic*. Very often, the inclusions of the competing phase are not static, but rather dynamic, slightly moving, changing their shapes, disappearing and again appearing. This fluctuating nature of the germs suggests to call them *heterophase fluctuations*.



**Fig. 1** Schematic picture of a sample with mesoscopic phase separation.

The features of a fluctuating germ can be compared with the characteristic scales typical of condensed matter. Such typical spatial scales, in addition to the interparticle distance  $a$ , are the interaction radius  $r_{int}$  and mean-free path  $\lambda_{mfp}$ . The latter is estimated as

$$\lambda_{mfp} \sim \frac{1}{\rho r_{int}^2} \sim \frac{a^3}{r_{int}^2},$$

where  $\rho \sim a^{-3}$  is average density. The typical velocities are the particle velocity and sound velocity

$$v \sim s \sim \frac{k_B T_D a}{\hbar},$$

with  $T_D$  being Debye temperature. Then the related temporal scales are the interaction time  $t_{int}$  and local equilibration time  $t_{loc}$ ,

$$t_{int} \sim \frac{r_{int}}{v}, \quad t_{loc} \sim \frac{\lambda_{mfp}}{v}.$$

In condensed matter, the characteristic spatial scales are of order

$$a \sim r_{int} \sim \lambda_{mfp} \sim 10^{-8} \text{ cm}.$$

Debye temperature can be estimated as  $T_D \sim 100 \text{ K}$ , which defines the typical velocities  $v \sim s \sim 10^5 \text{ cm/s}$  and temporal scales

$$t_{int} \sim t_{loc} \sim 10^{-13} \text{ s}.$$

The typical size of a heterophase fluctuation is  $l_f \sim 10 - 100 \text{ \AA}$ , hence the typical temporal scale is

$$t_f \sim \frac{l_f}{v} \sim 10^{-12} \div 10^{-11} \text{ s}.$$

This tells us that the heterophase fluctuations are usually also mesoscopic in time, being between the local-equilibration time and experimental observation time  $t_{exp}$ , such that

$$t_{loc} \ll t_f \ll t_{exp}.$$

Such nanoscale phase separation has been observed in high-temperature superconductors [1–3], ferroelectrics [4–7], around many structural phase transitions [8–11], in macromolecular assemblies [12], and at liquid-glass transitions [13]. More references can be found in review articles [14–16]. In the present paper, we concentrate on the study of heterophase ferroelectrics, in which inside ferroelectric phase there exist paraelectric nanoscale bubbles.

## 2 Phase Separation Description

Mathematically, the general situation, when the sample is phase separated, can be described in the following way [14–16]. Let the phases be enumerated by the index  $\nu = 1, 2, \dots$ . At a given snapshot, the system space  $\mathbb{V}$  is separated into subspaces  $\mathbb{V}_\nu$ , occupied by the related phases and forming an orthogonal covering  $\{\mathbb{V}_\nu\}$ , such that

$$\mathbb{V} = \bigcup_{\nu} \mathbb{V}_\nu. \quad (1)$$

The corresponding subvolumes sum to the total system volume

$$V = \sum_{\nu} V_{\nu} \quad (V_{\nu} \equiv \text{mes} \mathbb{V}_{\nu}). \quad (2)$$

The separation of thermodynamic phases can be done by means of an equimolecular surface [17, 18], when the total number of particles is the sum

$$N = \sum_{\nu} N_{\nu}. \quad (3)$$

The spatial location of the phases is fixed by the manifold indicator functions

$$\xi_{\nu}(\mathbf{r}) = \begin{cases} 1, & \mathbf{r} \in \mathbb{V}_{\nu} \\ 0, & \mathbf{r} \notin \mathbb{V}_{\nu} \end{cases}. \quad (4)$$

The overall phase configuration is described by the collection

$$\xi \equiv \{\xi_{\nu}(\mathbf{r}) : \nu = 1, 2, \dots; \mathbf{r} \in \mathbb{V}\}. \quad (5)$$

Under a given phase configuration, the statistical operator  $\hat{\rho}(\xi)$  can be found from the principle of minimal information, keeping in mind the normalization condition

$$\text{Tr} \int \hat{\rho}(\xi) \mathcal{D}\xi = 1, \quad (6)$$

where the trace operation is over the quantum degrees of freedom, while the functional integration is over the manifold indicator functions that play the role of random variables. Also, there is the definition of the internal energy

$$E = \text{Tr} \int \hat{\rho}(\xi) H(\xi) \mathcal{D}\xi, \quad (7)$$

which is the average of a Hamiltonian  $H(\xi)$ . The information functional has the form

$$\begin{aligned} I[\hat{\rho}(\xi)] &= \text{Tr} \int \hat{\rho}(\xi) \ln \frac{\hat{\rho}(\xi)}{\rho_0(\xi)} \mathcal{D}\xi + \\ &+ \alpha \left[ \text{Tr} \int \hat{\rho}(\xi) \mathcal{D}\xi - 1 \right] + \\ &+ \beta \left[ \text{Tr} \int \hat{\rho}(\xi) H(\xi) \mathcal{D}\xi - E \right], \end{aligned} \quad (8)$$

where the first term is the Kullback-Leibler information [19, 20],  $\alpha$  and  $\beta$  are the Lagrange multipliers guaranteeing the validity of conditions (6) and (7), and  $\hat{\rho}_0$  is a prior statistical operator taking into account additional prior information on the system, when it is available. If no additional apriori information is provided, the prior statistical operator is proportional to unity operator.

Minimizing the information functional yields the statistical operator

$$\hat{\rho}(\xi) = \frac{\hat{\rho}_0(\xi) \exp\{-\beta H(\xi)\}}{\text{Tr} \hat{\rho}_0(\xi) \exp\{-\beta H(\xi)\}}. \quad (9)$$

And the system thermodynamic potential, say free energy, writes as

$$F = -T \ln \text{Tr} \int \hat{\rho}_0(\xi) \exp\{-\beta H(\xi)\} \mathcal{D}\xi, \quad (10)$$

where  $\beta T = 1$ . All thermodynamic properties of the heterophase system can be defined if the thermodynamic potential can be calculated.

In (10) and in what follows, we set the Planck and Boltzmann constants as unity.

### 3 Averaging over Phase Configurations

The averaging over phase configurations is represented by the functional integration over the manifold indicator functions. In order to accomplish calculations involving this integration, it is necessary to explicitly define the corresponding functional measure.

Let us introduce for each subspace  $\mathbb{V}_\nu$  an orthogonal subcovering  $\{\mathbb{V}_{\nu i}\}$ , such that

$$\mathbb{V}_\nu = \bigcup_{i=1}^{n_\nu} \mathbb{V}_{\nu i}. \quad (11)$$

Then the manifold indicator (4) can be written as the sum

$$\xi_\nu(\mathbf{r}) = \sum_{i=1}^{n_\nu} \xi_{\nu i}(\mathbf{r} - \mathbf{a}_{\nu i}), \quad (12)$$

with the submanifold indicators

$$\xi_{\nu i}(\mathbf{r}) = \begin{cases} 1, & \mathbf{r} \in \mathbb{V}_{\nu i} \\ 0, & \mathbf{r} \notin \mathbb{V}_{\nu i} \end{cases}. \quad (13)$$

Snapshot phase weights are given by the integrals

$$\xi_\nu \equiv \frac{1}{V} \int \xi_\nu(\mathbf{r}) d\mathbf{r} = \int \xi_\nu(\mathbf{r}) \mathcal{D}\xi, \quad (14)$$

satisfying the normalization conditions

$$\sum_\nu \xi_\nu = 1, \quad 0 \leq \xi_\nu \leq 1, \quad (15)$$

which defines the set  $\{\xi_\nu\}$  as a probability measure. The differential measure over the set of all possible configurations is

$$\mathcal{D}\xi = \delta\left(\sum_\nu \xi_\nu - 1\right) \prod_\nu d\xi_\nu \prod_\nu \prod_{i=1}^{n_\nu} \frac{d\mathbf{a}_{\nu i}}{V}, \quad (16)$$

under the asymptotic condition  $n_\nu \rightarrow \infty$ .

Defining an effective Hamiltonian  $\tilde{H}$  by the relation

$$\exp(-\beta \tilde{H}) = \int \hat{\rho}_0(\xi) \exp\{-\beta H(\xi)\} \mathcal{D}\xi \quad (17)$$

makes it straightforward to rewrite the thermodynamic potential (10) in the simple form

$$F = -T \ln \text{Tr} e^{-\beta \tilde{H}}, \quad (18)$$

where  $\beta T = 1$ . This potential depends on the geometric phase probabilities  $w_\nu$  that are the minimizers of the thermodynamic potential,

$$F = F(\{w_\nu\}) = \text{abs min}_{\{\xi_\nu\}} F(\{\xi_\nu\}). \quad (19)$$

The phase probabilities satisfy the normalization condition

$$\sum_\nu w_\nu = 1, \quad 0 \leq w_\nu \leq 1. \quad (20)$$

Thus, defining the effective Hamiltonian by relation (17), we reduce the problem for a nonuniform system to the consideration of an effective uniform system with an effective Hamiltonian  $\tilde{H}$ .

### 4 Model of Heterophase Ferroelectric

Now we apply the above techniques for considering a heterophase ferroelectric that consists of a ferroelectric matrix with nanoscopic inclusions of paraelectric bubbles. The latter are randomly distributed in the sample volume, with no prior information on their locations being available. Recall that heterophase fluctuations are known to exist in many ferroelectrics [4–7, 21], such as, e.g., HCl and HCl-DCI. For concreteness, we consider here the ferroelectrics of the order-disorder KDP type [22], although a similar consideration can be realized for the ferroelectrics of displacement type.

The derivation of the Hamiltonian for a ferroelectric of the KDP type is similar to that for a double-well optical lattice filled by cold atoms [23–25]. Accomplishing the averaging over phase configurations, as described above, we come to the effective Hamiltonian

$$\tilde{H} = H_1 \oplus H_2, \quad (21)$$

with the phase components

$$H_\nu = w_\nu \sum_j (K_j - \Omega S_j^x - B_0 S_j^z) + w_\nu^2 \sum_{i \neq j} \left( \frac{1}{2} A_{ij} + B_{ij} S_i^x S_j^x - I_{ij} S_i^z S_j^z \right). \quad (22)$$

Here  $K_j$  is a single-site energy (a matrix element of kinetic energy),  $\Omega$  is tunneling frequency,  $B_0$  is a strain

field caused by external forces,  $A_{ij}$  is a matrix element of direct particle interactions, and  $B_{ij}$  and  $I_{ij}$  are matrix elements of exchange interactions. The quasi-spin operators have the following meaning. The operator  $S_j^x$  describes particle tunneling between the wells of a double well potential in a  $j$ -th lattice site. The operator  $S_j^y$  corresponds to the Josephson current between the wells. And the operator  $S_j^z$  characterizes the particle imbalance of the wells. The factors  $w_\nu$  are the phase probabilities defined in the previous sections. Each term  $H_\nu$  acts on a weighted Hilbert space  $\mathcal{H}_\nu$ , with the total Hamiltonian (21) acting on the fiber space

$$\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2. \quad (23)$$

The value of  $B_{ij}$  is usually much smaller than that of  $I_{ij}$ ,

$$|B_{ij}| \ll |I_{ij}|, \quad (24)$$

because of which it can be omitted.

Since there are two thermodynamic phases, there exist two order parameters

$$s_\nu \equiv \frac{2}{N} \sum_j \langle S_j^z \rangle_\nu \quad (\nu = 1, 2), \quad (25)$$

describing an average particle imbalance in each phase, where

$$\langle S_j^z \rangle_\nu = \frac{\text{Tr}_{\mathcal{H}_\nu} S_j^z \exp(-\beta H_\nu)}{\text{Tr}_{\mathcal{H}_\nu} \exp(-\beta H_\nu)}.$$

Ferroelectric phase enjoys a larger order parameter,

$$s_1 > s_2. \quad (26)$$

When there is no external strain, then

$$s_2 = 0 \quad (B_0 = 0), \quad (27)$$

which implies the absence of polarization in paraelectric phase, when there are no external fields [21, 26].

To realize explicit calculations, we need to invoke a decoupling for the quasi-spin operators. Here we resort to the Kirkwood decoupling [27] having the form

$$S_i^\alpha S_j^\beta = g_{ij}^\nu \left[ \langle S_i^\alpha \rangle_\nu S_j^\beta + S_i^\alpha \langle S_j^\beta \rangle_\nu - \langle S_i^\alpha \rangle_\nu \langle S_j^\beta \rangle_\nu \right], \quad (28)$$

in which  $g_{ij}^\nu$  characterizes particle correlations. In ferroelectric phase, the correlations are long-ranged, while in paraelectric phase, they are short-ranged.

For what follows, we need the notation for the correlation parameter

$$g_\nu \equiv \frac{\sum_{i \neq j} I_{ij} g_{ij}^\nu}{\sum_{i \neq j} I_{ij}} \quad (29)$$

and also the notations

$$u \equiv \frac{A}{J}, \quad h \equiv \frac{B_0}{J}, \quad (30)$$

where

$$A \equiv \frac{1}{N} \sum_{i \neq j} A_{ij}, \quad J \equiv \frac{1}{N} \sum_{i \neq j} I_{ij}.$$

The dimensionless parameter  $u$  characterizes direct disordering interactions, as compared to exchange ordering interactions, while the parameter  $h$  defines the strength of external strain.

## 5 Phonon degrees of freedom

Phonons play an important role in ferroelectrics. The related collective excitations can be introduced in the way that has been used for defining phonons in quantum crystals [28] or in optical lattices [29].

The interaction terms in Hamiltonian (22) are assumed to depend on the locations of particles as  $A(\mathbf{r}_i - \mathbf{r}_j)$  and  $I(\mathbf{r}_i - \mathbf{r}_j)$ . Each particle location is represented as

$$\mathbf{r}_j = \mathbf{a}_j + \mathbf{u}_j, \quad (31)$$

where

$$\mathbf{a}_j \equiv \langle \mathbf{r}_j \rangle_\nu, \quad \langle \mathbf{u}_j \rangle_\nu = 0. \quad (32)$$

Then the difference between the locations of two particles writes as

$$\mathbf{r}_{ij} \equiv \mathbf{r}_i - \mathbf{r}_j = \mathbf{a}_{ij} + \mathbf{u}_{ij},$$

$$\mathbf{a}_{ij} \equiv \mathbf{a}_i - \mathbf{a}_j, \quad \mathbf{u}_{ij} \equiv \mathbf{u}_i - \mathbf{u}_j.$$

Keeping in mind that the deviations of particles from their lattice sites are small, the interaction terms are expanded in powers of the deviations, limiting ourselves by the second-order powers, which gives

$$A(\mathbf{r}_{ij}) \cong A_{ij} + \sum_\alpha A_{ij}^\alpha u_{ij}^\alpha - \frac{1}{2} \sum_{\alpha\beta} A_{ij}^{\alpha\beta} u_{ij}^\alpha u_{ij}^\beta,$$

where

$$A_{ij} \equiv A(\mathbf{a}_{ij}), \quad A_{ij}^\alpha \equiv \frac{\partial A_{ij}}{\partial a_i^\alpha}, \quad A_{ij}^{\alpha\beta} \equiv \frac{\partial^2 A_{ij}}{\partial a_i^\alpha \partial a_j^\beta}.$$

Then Hamiltonian (22) transforms into

$$H_\nu = w_\nu \sum_j (K_j - \Omega S_j^x - B_0 S_j^x) +$$

$$\begin{aligned}
& + \frac{1}{2} w_\nu^2 \sum_{i \neq j} \left( A_{ij} - \frac{1}{2} \sum_{\alpha\beta} A_{ij}^{\alpha\beta} u_{ij}^\alpha u_{ij}^\beta \right) - \\
& - w_\nu^2 \sum_{i \neq j} \left( I_{ij} + \sum_{\alpha} I_{ij}^\alpha u_{ij}^\alpha - \frac{1}{2} \sum_{\alpha\beta} I_{ij}^{\alpha\beta} u_{ij}^\alpha u_{ij}^\beta \right) S_{ij}^z, \quad (33)
\end{aligned}$$

with the notation

$$S_{ij}^z \equiv S_i^z S_j^z. \quad (34)$$

Phonon and quasi-spin variables are decoupled so that to yield

$$\langle u_{ij}^\alpha u_{ij}^\beta S_{ij}^\gamma \rangle_\nu = \langle u_{ij}^\alpha u_{ij}^\beta \rangle_\nu \langle S_{ij}^\gamma \rangle_\nu. \quad (35)$$

The phonon spectrum is defined by the eigenproblem

$$\frac{w_\nu}{m} \sum_{j(\neq i)} \sum_{\beta} \Phi_{ij}^{\alpha\beta} e^{i\mathbf{k} \cdot \mathbf{a}_{ij}} e_{ks}^\beta = \omega_{ks}^2 e_{ks}^\alpha, \quad (36)$$

with the renormalized matrix

$$\Phi_{ij}^{\alpha\beta} \equiv A_{ij}^{\alpha\beta} - 2I_{ij}^{\alpha\beta} \langle S_{ij}^z \rangle_\nu. \quad (37)$$

Here  $\mathbf{e}_{ks}$  is a polarization vector, with  $s$  being the polarization index.

The phonon destruction and creation operators are introduced by the relations

$$\begin{aligned}
\mathbf{p}_j &= -\frac{i}{\sqrt{2N}} \sum_{ks} \sqrt{m\omega_{ks}} \mathbf{e}_{ks} (b_{ks} - b_{-ks}^\dagger) e^{i\mathbf{k} \cdot \mathbf{a}_j}, \\
\mathbf{u}_j &= \mathbf{v}_j + \frac{1}{\sqrt{2N}} \sum_{ks} \frac{\mathbf{e}_{ks}}{\sqrt{m\omega_{ks}}} (b_{ks} + b_{-ks}^\dagger) e^{i\mathbf{k} \cdot \mathbf{a}_j}. \quad (38)
\end{aligned}$$

Notice that the second transformation is nonuniform, which is necessary for getting rid of the terms linear in the operators  $b_{ks}$ , as is discussed in [30]. In the present case,

$$v_f^\alpha = -\frac{w_\nu}{2N} \sum_{i \neq j} \sum_{\beta} \gamma_{fj}^{\alpha\beta} I_{ij}^\beta S_{ij}^z,$$

with

$$\gamma_{jf}^{\alpha\beta} \equiv 4 \sum_{ks} \frac{e_{ks}^\alpha e_{ks}^\beta}{m\omega_{ks}^2} e^{i\mathbf{k} \cdot \mathbf{a}_{jf}}.$$

Then Hamiltonian (33) reduces to the sum

$$H_\nu = E_\nu + H_\nu^{ph} + H_\nu^{ps} + H_\nu^{ind}. \quad (39)$$

The first term here is

$$E_\nu = \frac{1}{2} w_\nu^2 N A - w_\nu^2 \sum_{i \neq j} \sum_{\alpha\beta} I_{ij}^{\alpha\beta} \langle S_{ij}^z \rangle_\nu \langle u_j^\alpha u_j^\beta \rangle_\nu. \quad (40)$$

The second term is the phonon Hamiltonian

$$H_\nu^{ph} = w_\nu \sum_{ks} \omega_{ks} \left( b_{ks}^\dagger b_{ks} + \frac{1}{2} \right). \quad (41)$$

The third term is the pseudospin Hamiltonian

$$H_\nu^{ps} = -w_\nu \sum_j (\Omega S_j^x + B_0 S_j^z) - w_\nu^2 \sum_{i \neq j} \tilde{I}_{ij} S_{ij}^z, \quad (42)$$

with the renormalized interaction

$$\tilde{I}_{ij} \equiv I_{ij} - \sum_{\alpha\beta} I_{ij}^{\alpha\beta} \langle u_j^\alpha u_j^\beta \rangle_\nu. \quad (43)$$

And the last term in (39) is the four-spin Hamiltonian induced by the interactions of quasi-spins through particle oscillations,

$$H_\nu^{ind} = -\frac{w_\nu^3}{N} \sum_{i \neq j} \sum_{f \neq g} \Gamma_{ijfg} S_{ij}^z S_{fg}^z, \quad (44)$$

with the vertex

$$\Gamma_{ijfg} \equiv \sum_{\alpha\beta} I_{ij}^{\alpha\beta} \gamma_{jf}^{\alpha\beta} I_{fg}^\beta.$$

It is possible to show that the induced shift  $\mathbf{v}_j$  as well as the induced Hamiltonian are small [16]. In the long-wave approximation, we have

$$\mathbf{v}_j \cong 0, \quad H_\nu^{ind} \cong 0.$$

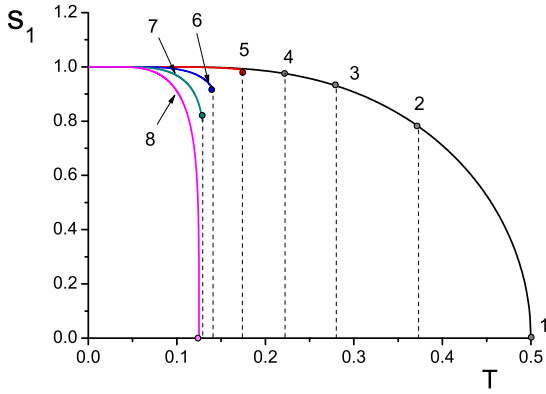
Therefore the deviation-deviation correlation function becomes

$$\langle u_i^\alpha u_j^\beta \rangle_\nu = \frac{\delta_{ij}}{2N} \sum_{ks} \frac{e_{ks}^\alpha e_{ks}^\beta}{m\omega_{ks}} \coth \left( \frac{w_\nu \omega_{ks}}{2T} \right). \quad (45)$$

## 6 Properties of Heterophase Ferroelectrics

To study the properties of the heterophase ferroelectric, we accomplish numerical calculations for the model of Sec. 4. The quasi-spin variables are treated in the Kirkwood approximation (28), with the correlation parameters  $g_1 = 1$  and  $g_2 \ll 1$ . Also we take into account that  $\Omega \ll J$ . The phase probability  $w_\nu$  is defined as the minimizer of the free energy (18), according to conditions (19) and (20).

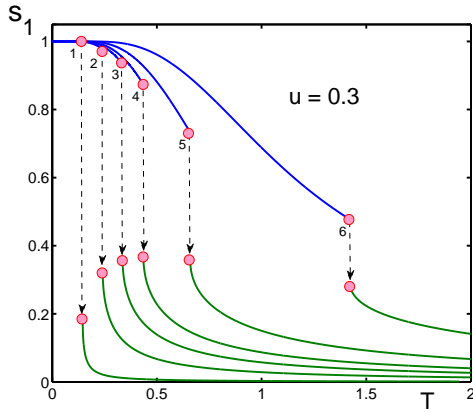
Figure 2 shows the temperature behavior of the ferroelectric order parameter  $s_1$  in the absence of external strain,  $h = 0$ , for different disorder parameters  $u$ . Temperature is measured in units of the exchange interaction strength  $J$ . The existence of the mesoscopic paraelectric germs inside the ferroelectric matrix makes the phase transition ferroelectric-paraelectric of first order for the disorder parameters in the interval  $0 < u <$



**Fig. 2** Ferroelectric order parameter  $s_1$ , in the absence of strain,  $h = 0$ , as a function of temperature  $T$ , in units of  $J$ , for different disorder parameters: (1)  $u = 0$ ; (2)  $u = 0.1$ ; (3)  $u = 0.3$ ; (4)  $u = 0.4$ ; (5)  $u = 0.51$ ; (6)  $u = 0.75$ ; (7)  $u = 1$ ; (8)  $u = 1.5$ . The points mark the temperatures of ferroelectric-paraelectric phase transitions.

3/2. The phase transition temperature is in the range  $0.125 < T_c < 0.5$ .

Figure 3 demonstrates the influence of the external strain  $h$  for the fixed disorder parameter  $u = 0.3$ . The phase transition for this  $u$  is of first order, but the strain makes  $s_1$  nonzero above the transition point.



**Fig. 3** Ferroelectric order parameter  $s_1$ , as a function of temperature, in units of  $J$ , for fixed disorder parameter  $u = 0.3$  and varying external strain: (1)  $h = 0.01$ ; (2)  $h = 0.1$ ; (3)  $h = 0.2$ ; (4)  $h = 0.3$ ; (5)  $h = 0.5$ ; (6)  $h = 1$ . The corresponding first-order transition temperatures are: (1)  $T_0 = 0.145$ ; (2)  $T_0 = 0.241$ ; (3)  $T_0 = 0.336$ ; (4)  $T_0 = 0.436$ ; (5)  $T_0 = 0.660$ ; (6)  $T_0 = 1.422$ .

The sound velocity for a heterogeneous matter is expected to be lower than that of the pure phase. The isotropic part of the sound velocity writes as

$$s = \sum_{\nu} w_{\nu} s_{\nu}, \quad (46)$$

where

$$s_{\nu} \equiv \lim_{k \rightarrow 0} \frac{\omega_k}{k} \quad \left( \omega_k^2 = \frac{1}{3} \sum_{s=1}^3 \omega_{ks}^2 \right). \quad (47)$$

From Sec. 5, we have

$$s_{\nu} = \sqrt{w_{\nu}} c_{\nu} \quad \left( c_{\nu} \equiv \sqrt{\frac{D_{\nu}}{2m}} \right), \quad (48)$$

where  $D_{\nu}$  denotes the nearest-neighbor part of the dynamic matrix

$$D_{ij}^{\nu} \equiv -\frac{1}{3} \sum_{\alpha=1}^3 \Phi_{ij}^{\alpha\alpha}.$$

As a result, we get

$$s = w_1^{3/2} c_1 + w_2^{3/2} c_2. \quad (49)$$

Since  $w_{\nu} < 1$ , and taking into account that  $c_1 \approx c_2 \equiv c$ , it is seen that  $s < c$ . The maximal attenuation of the sound velocity occurs at the transition point, where  $w_1 \approx 0.5$ . Then the relative decrease of the sound velocity, caused by heterophase fluctuations, is  $\delta s \equiv (s - c)/c \approx -0.293$ .

The mesoscopic heterophase inclusions increase the mean-square deviation of particles

$$r_{\nu}^2 \equiv \sum_{\alpha} \langle u_i^{\alpha} u_i^{\alpha} \rangle_{\nu} = \frac{1}{2N} \sum_{ks} \frac{1}{m\omega_{ks}} \coth \frac{w_{\nu} \omega_{ks}}{2T}. \quad (50)$$

Thus, in the Debye approximation, when

$$\omega_{ks} \equiv \omega_k = s_{\nu} k \Theta(k_D - k), \quad (51)$$

with the Debye radius defined by the expression  $k_D^3 = 6\pi^2 \rho$ , the mean-square deviation is

$$r_{\nu}^2 = \frac{18T^2 w_{\nu}}{m\Theta_{\nu}^3} \int_0^{\Theta_{\nu}/2T} x \coth x \, dx, \quad (52)$$

where the effective Debye temperature is

$$\Theta_{\nu} \equiv w_{\nu} s_{\nu} k_D = w_{\nu}^{3/2} T_{\nu D} \quad (T_{\nu D} \equiv c_{\nu} k_D). \quad (53)$$

At relatively low or high temperature, one has

$$r_{\nu}^2 \simeq \begin{cases} 9w_{\nu}/4m\Theta_{\nu}, & T \ll \Theta_{\nu} \\ 9w_{\nu}T/m\Theta_{\nu}^2, & T \gg \Theta_{\nu} \end{cases}.$$

This shows that the  $\nu$ -th phase can be treated as localized only when its weight is sufficiently large, so that  $r_{\nu} > a$ . Otherwise, the particles cannot be localized, experiencing strong diffusion [31], hence cannot form localized heterophase germs.



The increase of the mean-square deviation influences the value of the Debye-Waller factor that, for a heterophase system, has the form

$$f_{DW} = \sum_{\nu} w_{\nu} f_{\nu}, \quad (54)$$

where

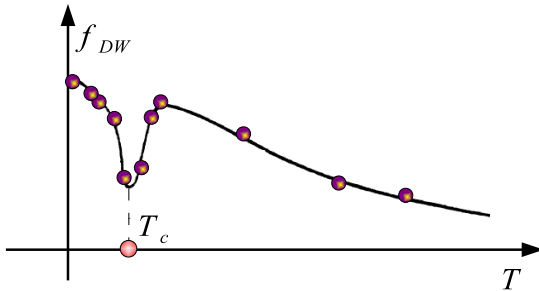
$$f_{\nu} = \exp\left(-\frac{1}{3} k_0^2 r_{\nu}^2\right).$$

The same expression is valid for the Mössbauer effect probability [32].

The latter, with the notation for the recoil energy  $E_R \equiv k_0^2/2m$  reads as

$$f_{\nu} = \exp\left(-\frac{2}{3} m E_R r_{\nu}^2\right). \quad (55)$$

The typical behavior of the Debye-Waller factor (54) is shown in Fig. 4. At the transition temperature, the factor exhibits the so-called *cusped-shaped anomaly*. The corresponding relative sagging is about 30%, as compared to the value just above  $T_c$ .



**Fig. 4** Debye-Waller factor as a function of temperature, exhibiting the typical cusped-shaped anomaly at  $T_c$ , caused by the arising heterophase fluctuations.

This behavior is in good agreement with the Debye-Waller factor (or Lamb-Mössbauer factor) of many ferroelectrics, displaying the cusped-shaped anomaly at  $T_c$ . First, it has been observed for  $\text{BaTiO}_3$  and  $\text{PbTiO}_3$  at a weak first-order phase transition [33–35] and later for many other ferroelectrics and antiferroelectrics, as well as at magnetic transitions, structural transitions, and high-temperature superconducting transitions [36–41]. Initially, one tried to connect such cusped-shaped anomalies with the existence of soft modes. However, by accurate microscopic treatments, it has been proved that soft modes are able to account for only about 1% of change in the Debye-Waller factor and cannot be related to such a large anomaly as a 30% sagging of the factor [42–44]. But the cusped-shaped anomaly can be explained by the presence of heterophase fluctuations, as is shown above.

## 7 Conclusion

We have presented a theory of ferroelectrics, inside which there exist fluctuating germs of paraelectric phase. The appearance of such heterophase fluctuations essentially influences the properties of the matter. For instance, the sound velocity decreases, the mean-square deviation increases, and the Debye-Waller factor experiences a cusped-shaped anomaly at the point of a phase transition. The described cusped-shaped anomaly is in good agreement with experiments. The presented method of describing heterophase fluctuations can be employed for other types of condensed matter, e.g., for high temperature superconductors [45].

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